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FULL LENGTH ARTICLE

Removal of cadmium from aqueous solution using marine green algae, *Ulva lactuca*

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Abstract The present study aimed to evaluate the efficiency of marine algae for removal of metals from the aqueous solution. The green alga, *Ulva lactuca*, collected from the intertidal zone of the Suez Bay, northern part of the Red Sea was used to reduce cadmium levels from the aqueous solutions. The biosorption mechanisms of Cd^{2+} ions onto the algal tissues were examined using various analytical techniques: Fourier-transform infrared spectroscopy (FT-IR) and Scanning electron microscopy (SEM). Results indicated that at the optimum pH value of 5.5; about 0.1 g of *U. lactuca* was enough to remove 99.2% of 10 mg L^{-1} Cd^{2+} at 30 °C in the aqueous solutions. The equilibrium data were well fitted with the Langmuir and Freundlich isotherms. The monolayer adsorption capacity was 29.1 mg g^{-1}. The calculated R_L and '*n*' values have proved the favorability of cadmium adsorption onto *U. lactuca*. The desorption test revealed that HCl was the best for the elution of metals from the tested alga. In conclusion, the seaweed *U. lactuca* was the favorable alternative of cadmium removal from water.

Introduction

Environmental pollution due to toxic heavy metals is a significant worldwide problem due to their incremental accumulation in the food chain and continued persistence in the ecosystem (Aneja et al., 2010). The removal and recovery of toxic heavy metal ions from wastewaters are of great importance from an environmental viewpoint. The major sources of Cd(II) release into the environment through wastewater streams are electroplating, smelting, paint pigments, batteries, fertilizers, mining and alloy industries (Iqbal and Edyvean, 2005).

Cadmium is one of the toxic heavy metals with a greatest potential hazard to humans and the environment. It causes kidney damage, bone diseases and cancer. Chronic exposure to elevated levels of cadmium is known to cause renal dysfunction, bone degeneration and liver damage (Iqbal et al., 2007).

Conventional techniques for removing heavy metals from industrial effluents include chemical precipitation, chemical reduction, adsorption, ion exchange, evaporation and

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membrane processes, while the biosorption process offers potential advantages such as low operating cost, minimization of chemical or biological sludge, high efficiency of heavy metal removal from diluted solutions, regeneration of biosorbents, possibility of metal recovery and being environmentally friendly (Ahluwalia and Goyal, 2007).

Biosorption is an innovative technology using living or dead biomasses to remove toxic metals from aqueous solutions. Various biomasses such as bacteria, yeast, fungi and alga for biosorption of metal ions have been widely used (Vieira and Volesky, 2000). Among the biological materials, marine alga have high metal binding capacities due to the presence of polysaccharides, proteins or lipid in the cell wall structure (Davis et al., 2003). The mechanism of biosorption is mainly based on physical adsorption (electrostatic attraction–Vanderwaal forces of attraction) and/or chemical adsorption (covalent binding between negative charge of cell surface and cationic ions (Vijayaraghavan and Yun, 2008). The physiochemical phenomena besides being rapid are reversible (Darnall et al., 1986).

The main objective of this study was to evaluate the biosorption performance of locally marine macroalga *Ulva lactuca* for the removal of cadmium ions from aqueous solutions, as well as to study the effect of pH, biomass amount, time, initial metal concentration and temperature on the treatment process. Langmuir and Freundlich isotherm equations were employed to quantify the biosorption equilibrium. In addition to study the efficiency of different elutants to desorp the cadmium from the algae tissues.

Materials and methods

Materials

Preparation of cadmium

The analytical grade salt $Cd(NO_3)_2$ was used to prepare stock solution (1000 mg L^{-1}) of Cd^{2+}. The desired concentrations were prepared by dilution of the stock solution with deionised water. The initial pH was adjusted with concentrated HCl or NaOH. The initial metal concentration (10 mg L^{-1}) was measured using a flame atomic absorption spectroscopy (Perkin Elmer AAnalyst 100). Samples were diluted before the required analysis to set the calibration linear range.

Preparation of adsorbent

U. lactuca (green alga) was collected from the Suez Bay shore. The collected alga was washed with excess tap water and finally with distilled water to remove salt and particulate materials from the surface, dried at room temperature, then ground as powder using an electrical mill and sieved to uniform particle sizes (0.210 mm).

Methods

Effect of pH

During the experiment of pH effect, the parameters of temperature, solution volume, biosorbent amount, initial metal ion concentration, and shaking time were fixed at 30 °C, 10 mL, 10 mg L^{-1}, 0.1 g and 120 min, respectively. Effects of pH were tested at pH 2, 3, 4, 5, 5.5, 6 and 8 (Karaca, 2008).

Effect of biomass amount

This part of the experiment was performed to verify the effect of biosorbent weight on the sorption process. Different weights of biosorbents (0.05, 0.1, 0.2 and 0.4 g) were mixed and shaken with 10 mL solution of 10 mg Cd/L at 30 °C, pH 5.5 for 120 min (Ajaykumar et al., 2008).

Initial cadmium concentration

The extent of removal of heavy metals from aqueous solution depends strongly on the initial metal concentration. In order to assess, different Cd concentrations of 3, 5, 7, 10, 25, 50, 75 and 100 mg/L were examined at constant parameters, pH 5.5 with 0.1 g of biosorbent added into 10 ml solutions at 30 °C (Meral Karaca, 2008).

Effect of temperature

Biosorption process was carried out at different values of temperature (20, 25, 30 and 35 °C), at constant pH 5.5, 0.1 g biosorbent weight, volume of 10 ml of 10 mg Cd/L for 120 min (Ajaykumar et al., 2008).

Metal removal efficiency

Biosorption capacity (q_e), the amount of metal adsorbed per gram of biosorbent, can be calculated at equilibrium in mg/g as follows:

$$q_e = (C_0 - C_e)V/m \quad (1)$$

where C_0 is the initial concentration of metal ions in the solution (mg/L), C_e is the equilibrium concentration of metal ions in the solution (mg/L), V is the volume of solution (in L) and m is the mass of biosorbent applied (in g) (Hashim and Chu, 2004). Metal uptake can also be displayed by the percentage of metal removal given by (Zhang et al., 1998; Volesky, 1992):

$$\text{Metal removal } (\%) = 100(C_0 - C_e)/C_0 \quad (2)$$

Cadmium measurement

The collected samples from different experiments were filtered with filter paper (47 μm) and Cd^{2+} concentration was measured by an Atomic Absorption Spectrometer (Perkin Elmer AAnalyst 100). The analyses were carried out at the wavelengths of 228.8 nm.

Characterization of biomass

Fourier-transform infrared analysis (FTIR)

Dry *U. lactuca* samples (before and after cadmium biosorption) were examined with a Model Tensor – 27. Bruker FTIR within the wave number 200–5000 cm^{-1} under ambient conditions. This technique was used to elucidate the chemical characteristics relevant to metallic ion sorption by the algal biomass (Raize et al., 2004).

Scanning electron microscopy (SEM)

Dry *U. lactuca* samples (before and after cadmium biosorption) were glued and coated with gold. The coated samples were put into a JEOL, JSM-52500 LV SEM, Japan and different sections

in the samples were examined. This technique was used to examine the algal cell surface (Saravanan et al., 2011).

Isotherm studies

Biosorbent (0.1 g) was added to 10 mL of metal solutions with different initial cadmium concentrations varying from 3 to 100 mg/L. The solution was controlled at pH 5.5, 30 °C and for 2 h (Ajaykumar et al., 2008).

Desorption of metals

Desorption studies were performed in a way that, 0.1 g of biosorbent was shaken with 10 mL of 10 mg/L cadmium ion solution for 5–30 min. After shaking and filtration steps, biosorbed metals were tried to be desorbed in separate experiments with 1 M HCl, 1 M H_2SO_4, 1 M HNO_3 and distilled water. Finally, the concentration of the metal ions in the filtrate was determined by AAS. The eluted metal was determined and the elution efficiency by desorption agent can be defined as follows:

$$\text{Elution efficiency } (\%) = 100(C_s V_s)/(q_e m) \quad (3)$$

where C_s is the concentration of metal ions in the desorbed solution (mg/L), V_s is the volume of solution in the desorption (L), m is the mass of biosorbent used in desorption studies (g) and q_e is defined in Eq. (1) (Nessim et al., 2011).

Results and discussion

Factors affecting biosorption of Cd^{2+}

Effect of pH

In order to demonstrate the effect of pH on biosorption of Cd(II) ions by algae, pH ranges of 2–8 were used and illustrated in Fig. 1. Biosorption of heavy metal ions is dependent on the pH of solution as it affects biosorbents surface charge, degree of ionization, and the species of biosorbent (Ahmady-Asbchin et al., 2008). The present results showed that, the metal removal percentage was increased up to pH 5.5 and then decreased. In contrast, when the pH was increased, a partial desorption of protons occurs allowing the sorption of Cd(II) onto the sites left by protons at the surface of biomass and the biosorption reached the maximum (91.9%) around pH 5.5. According to this, it may be suggested that there was a clear competition for the biomass sorption sites between Cd(II) and proton.The decrease in biosorption at higher pH values (pH > 5.5) may be attributed to that the amount of OH^- ions is increased in the solution, so metal ions react with OH^- ions and are precipitate as a metal hydroxide at high pH value (Farooq et al., 2010).

At higher pH, the removal was also low compared with the optimum condition. This can be explained as the binding site may not activate in basic conditions (Memon et al., 2008). Dursun (2006) concluded that, pH of the solution influences both metal binding sites on the cell surface and the chemistry of metal in solution.

Effect of biomass amount

It was observed that the amount of Cd^{2+} ions adsorbed varied with varying algae amounts (Fig. 2). The results recorded removal percentages of 86.6%, 99.2%, and 98.7% and 98.1% at weights of 0.05, 0.1, 0.2 and 0.4 g, respectively. It seems that the highest biosorption uptake was found at the biomass weight of 0.1 g. High biosorbent amounts are known to cause cell agglomeration and a consequent reduction in intercellular distance and produce 'screen effect' among a dense layer of cells, leading to the 'protection' of binding sites from metal ions (Pons and Fuste, 1993). The obtained data were in agreement with those of Esposito et al. (2001) and El-Sikaily et al. (2011), who reported lower biosorbed metal percentage (q) at high adsorbent concentrations.

Effect of initial Cd^{2+} concentration

The present data illustrated that, as the initial metal ion concentration increases the percentage of Cd^{2+} ions adsorption increases (Fig. 3). Removal percentage starts from 55% for 3 mg/L and increases up to 99.6% at 10 mg/L Cd^{2+} then decreases (steady state) as the initial heavy metal concentration increases. The increase in adsorption is a result of an increase in the driving forces, i.e. concentration gradient. At lower concentrations, all Cd^{2+} ions present in solution could interact with the binding sites and thus the percentage adsorption was increased gradually as Cd^{2+}concentration increases While, at higher concentrations than 10 mg/L Cd^{2+}, slightly lower adsorption yield is mainly attributed to the saturation of adsorption sites. This is due to an increase in the number of ions competing for available binding sites in the biomass (Puranik and Paknikar, 1999).

Effect of temperature

Effect of solution temperature (20, 25, 30 and 35 °C) on the biosorption of Cd^{2+} ions was investigated. Fig. 4 shows that when temperature was increased from 20 °C to 30 °C, the uptake of Cd^{2+} ions by *U. lactuca* was increased from

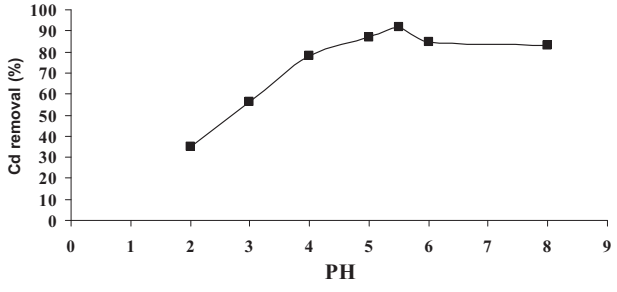

Figure 1 Effect of pH values on cadmium biosorption.

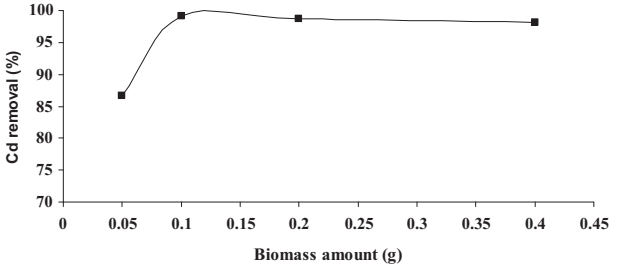

Figure 2 Effect of biomass amount on removal of cadmium.

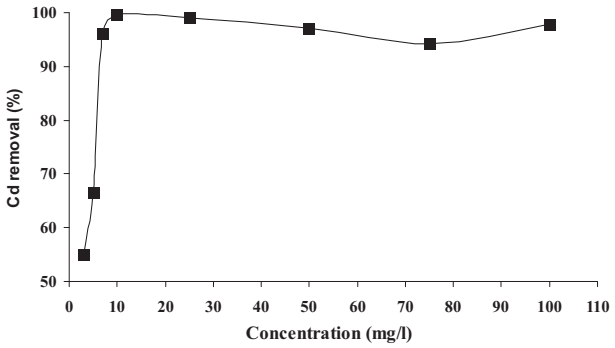

Figure 3 Effect of initial cadmium ions concentration on the biosorption.

63.14% to 87.3%. The temperature has two major effects on the adsorption process. The first is that increasing the temperature will increase the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbate particles because liquid viscosity decreases as the temperature constant increases. Second is that, the temperature affects the equilibrium capacity of the adsorbate depending on whether the process is exothermic or endothermic (Al-Qodah, 2006).

FTIR

FTIR analysis was carried out in order to identify the different functional groups present in *U. lactuca* which were responsible for the adsorption process (Fig. 5). The peaks appearing in the FTIR spectrum were assigned to various functional groups according to their respective wave numbers as reported in the literature. The shift in the band 3409 and 3414 cm^{-1} indicates changes in the hydroxyl and amino group positions during cadmium biosorption (Sheng et al., 2004). The peak observed at 2931 cm^{-1} (before and after biosorption) was associated with the stretching vibrations of C–H bond of methyl, methylene and methoxy groups (Feng et al., 2008). Intense band at 2285 cm^{-1} (before biosorption) indicates C–H stretching from CH_2 groups (Solomon et al., 2012), that peak disappeared after biosorption. The peaks at 1656 cm^{-1} (before biosorption) and 1640 cm^{-1} (after biosorption), corresponded to the C=C stretching which might be attributed to the presence of lignin aromatic bond (Florido et al., 2009). The peaks at 1431 cm^{-1} (before biosorption) reveal the presence of C–O (Fourest and Volesky, 1996). The presence of amide in the structure of alga is confirmed by the peak at 1542 cm^{-1} (after biosorption) (Sheng et al., 2004). Also, the bands at 1107 cm^{-1} (before biosorption) and 1053 cm^{-1} (after biosorption) corresponded to the C–O stretching of alcohol or carboxylic acid (Ngah and Hanafiah, 2007). The values which appeared in the region between 538 and 1030 are finger prints of the symmetric bond.

Scanning electron microscopy (SEM)

The morphology of *U. lactuca* surface was analyzed by scanning electron microscopy before and after cadmium loading (Fig. 6a and b). The cells before exposure were smooth and had certain dimensions, after their exposure to cadmium ions solution, they become destroyed and swollen, and their surface becomes meanders. This may be due to cadmium ions precipitated around the cell surface and linked with their functional groups. Also, these changes were probably caused when the samples were exposed to heavy metal solution; the metal ions replaced some of the cations initially present in the cell wall matrix and created stronger crosslinking. Due to ion-exchange mechanism, the heavy metal ions occupied the available free binding sites (Saravanan et al., 2011).

Biosorption isotherm models

The sorption isotherms are the mathematical model which provides an explanation about the behavior of adsorbate species between solid and liquid phases. Langmuir and Freundlich isotherm models (Langmuir, 1918 and Freundlich, 1906) were studied for the investigation of biosorption of Cd^{2+} ions by *U. lactuca* .The Langmuir isotherm assumes monolayer coverage of metal ions over a homogeneous sorbent surface (Sheng et al., 2004). The isotherm is presented by the following equation:

$$q_e = q_{max} b C_e / (1 + b C_e) \quad (4)$$

where q_e (mg/g) is the observed biosorption capacity at equilibrium, q_{max} (mg/g) is the maximum biosorption capacity corresponding to the saturation capacity (representing total binding sites of biomass), C_e (mg/L) is the equilibrium concentration and b (L/mg) is a coefficient related to the affinity between the sorbent and sorbate (b is the energy of adsorption). The linear relationship can be obtained by plotting $(1/q_e)$ vs. $(1/C_e)$:

$$1/q_e = 1/(b q_{max} C_e) + 1/q_{max} \quad (5)$$

In which b and q_{max} are determined from slope and intercept, respectively. The different biosorbents can be compared by its respective q_{max} values which are calculated from fitting the Langmuir isotherm model to actual experimental data.

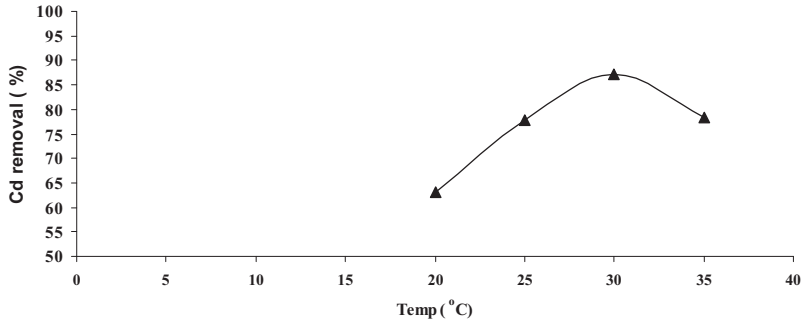

Figure 4 Effect of temperature on the biosorption of cadmium.

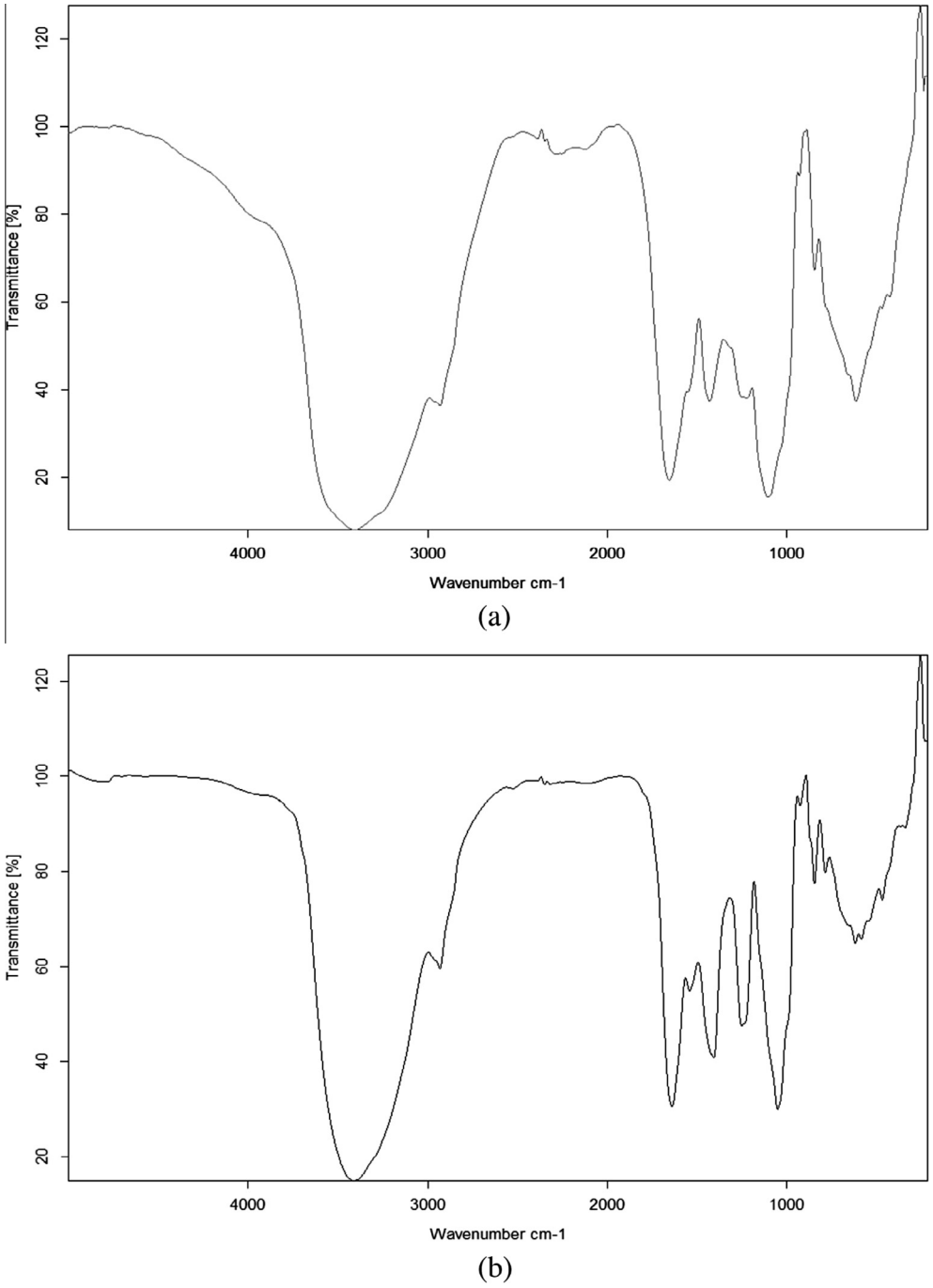

Figure 5 FTIR spectrum of *Ulva lactuca* (a) before biosorption and (b) after biosorption of cadmium.

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. This isotherm can be described as follows:

$$q_e = K_f C_e^{1/n} \tag{6}$$

where K_f and n are the Freundlich constants related to the adsorption capacity and intensity of the sorbent, respectively (Freundlich, 1906). The Freundlich model can be easily linearized by plotting it in a logarithmic form:

$$\log q_e = \log K_f + 1/n \log C_e \tag{7}$$

The plots of non-linearized Langmuir and Freundlich adsorption isotherms are shown in Figs. 7 and 8. The adsorption isotherm constants were determined by using non-linear regression. The Langmuir and Freundlich adsorption constants evaluated from the isotherms with the correlation coefficients are also presented in Table 1. The best-fit equilibrium model was determined based on the linear regression

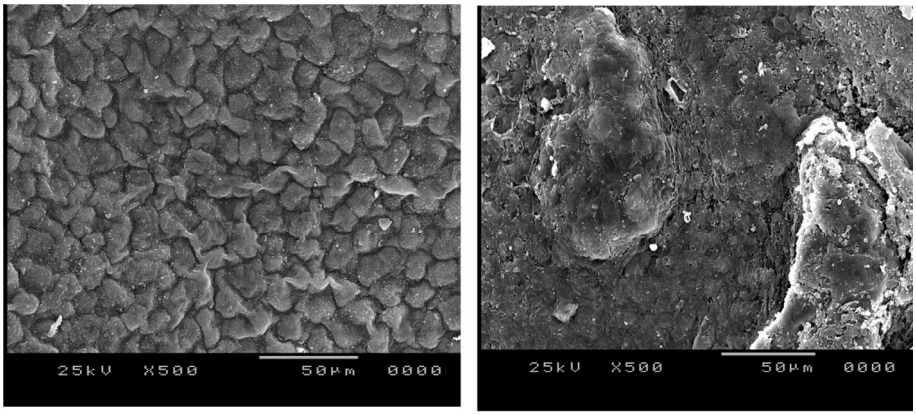

Figure 6 SEM micrograph (×5000) of *Ulva lactuca* cell wall (a) before and (b) after Cd^{2+} adsorption from aqueous solution.

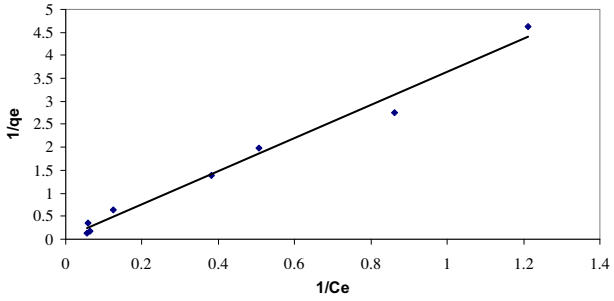

Figure 7 Langmuir isotherm plot for cadmium ions.

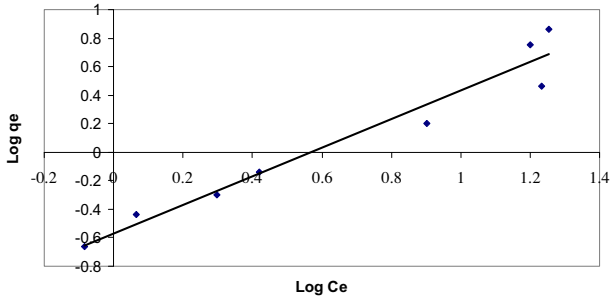

Figure 8 Freundlich isotherm plot for cadmium ions.

Table 1 Langmuir and Freundlich isotherm parameters for cadmium.

Model	Parameter			
Langmuir	q_{max}	b	R^2	R_L
	29.069	0.000545	0.984	0.802053
Freundlich	n	k_f	R^2	
	1.0002	0.2300	0.9517	

correlation coefficient R^2. The fitting of experimental data with the Langmuir model was emphasized by high R^2 values. The correlation regression coefficient (R^2 = 0.984) shows that the biosorption process is fit Langmuir model. The Langmuir fit is consistent with strong monolayer sorption on to specific sites.

Accordingly, the essential characteristics of the Langmuir isotherm parameter can be expressed in terms of a separation factor or a dimensionless equilibrium parameter, R_L according to the equation of Ahalya et al. (2005) and Kagaya et al. (2006) as follows:

$$R_L = 1/(1 + bC_0) \quad (8)$$

where b is the Langmuir constant and C_0 is the initial concentration of Cd^{2+} ions. The value of the separation parameter R_L provides important information about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). R_L values between 0 and 1 indicate favorable absorption (Mckay et al., 1982). From this study, The R_L was found to be 0.802053 (Table 1).

The experimental data obeyed also the Freundlich model, as confirmed by the high determination coefficient ($R^2 > 0.951$) (Table 1). As can be seen from the results, the n values were found to be 1.0002. According to Kadirvelu and Namasivayam (2000), n values between 1 and 10 represent beneficial biosorption. The 'n' value of Freundlich equation could give an indication on the favorability of sorption. K_f can serve as an indicator for the maximal metal cation uptake capacity of the algal biomass.

Desorption of metal ions

With the use of elutants it is necessary to evaluate both efficiency of desorption and preservation of biosorption capacity of the biomass (Chu et al., 1997). The adsorbed metals on adsorbents cannot be completely reversible as reported by several observations on the literature of workers (Farrah and Pickering, 1978; Brummer et al., 1988; Ainsworth et al., 1994). If desorbent fulfills the assigned criteria, it is possible to recover metal ions in the form of concentrated solution and to regenerate the biosorbent that can be used in another biosorption cycle.

Desorption of Cd(II) ions by *U. lactuca* biomass was studied by using 1 M of HCl, H_2SO_4 and HNO_3 as well as distilled water. The results of desorption are shown in Fig. 9, which

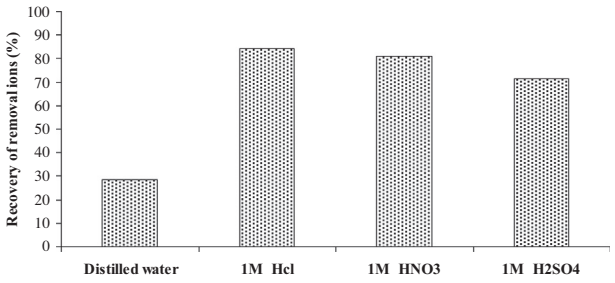

Figure 9 Effect of various agents on desorption of cadmium from *Ulva lactuca* biomass.

clearly indicate effective desorption with mineral acids (HCl and H_2SO_4). The distilled water has a low amount of Cd^{2+} ions recovery (< 28%). The highest amount of Cd^{2+} ions recovery was 84.1% using of 1 M HCl. While, for the other two elutants (HNO_3 and H_2SO_4), recovery percentages of 81% and 71.3% were observed, respectively. The rapid desorption kinetics elevated the applicability of the biosorption process. At acidic conditions, H^+ ions protonate the adsorbent surface by replacing the adsorbed metal ions on the adsorbent surface leading to desorption of the positively charged metal ion species (Karthikeyan et al., 2007).

Conclusions

The batch experiment conducted in this study focused on the biosorption of Cd(II) ions onto *U. lactuca* biomass from aqueous solution. The results showed that the dead biomass of green alga *U. lactuca* could be used as an efficient biosorbent material for the removal of cadmium ions from aqueous solutions. pH 5.5 was selected as a compromised point with removal percentage, 0.1 g biosorbents was achieved to highest removal percentage and initial Cd^{2+} concentration is more efficient in the range of 7 and 10 mg/L, with optimization temperature at 30 °C. The Langmuir and Freundlich adsorption models were used for the mathematical description of the biosorption equilibrium of cadmium ions to the dried biomass of alga. The obtained results showed that the adsorption equilibrium data fitted very well to both the Langmuir and Freundlich models. Data of the IR spectrum confirmed the presence of some functional groups in the biomass of *U. lactuca*. The desorption experiments suggested that the regeneration of the biosorbents was possible for repeated use especially with regard to Cd(II). Finally, it was concluded that *U. lactuca* can be used as an effective, low cost, and environmentally friendly biosorbent for removal of Cd(II) ions from aqueous solution.

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